Kinetics and Volumes of Activation of the Reactions of Nickel(II) and Cobalt(II) Ions with Some Uncharged Ligands in Water, Studied by a Laser Temperature-jump Method at High Pressures

By E. F. CALDIN,* M. W. GRANT, and B. B. HASINOFF

(*University Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent*)

Summary The volumes of activation $\Delta V^{\ddagger}$ for the reactions of Ni^{II} and Co^{II} ions with some uncharged ligands in water were determined from kinetic measurements in a laser temperature-jump apparatus, in which rates could be determined spectrophotometrically at pressures up to several kbar; the values are all *ca.* 7—9 cm^3 mol^{-1}.

THE ligand-substitutions of Co^{II} and Ni^{II} ions with the bidentate ligand pyridine-2-azo-*p*-dimethylaniline (pada) and with NH_3 in water have been studied by the temperature-jump method, at a series of pressures 1—2000 bar, with the aid of a laser temperature-jump apparatus already described.[1] A high-pressure cell with spectrophotometric detection was used; this was designed and constructed in collaboration with Dr. P. A. Tregloan, and is to be described later.[2]

The derived values of the volume of activation $\Delta V^{\ddagger}$ (see Table) are all *ca.* 7—9 cm^3 mol^{-1}, a value which corresponds to a considerable fraction of the molar volume of water. The values for the small ligand NH_3 and the bulky ligand pada

TABLE

Volumes of activation for formation of complexes at zero pressure

Cation	Ligand	T/°C	$\Delta V^{\ddagger}/cm^3\ mol^{-1}$
Ni^{2+}	NH_3	30·0	7·1 ± 1·0
Ni^{2+}	pada	49·0	8·2 ± 0·2
Co^{2+}	pada	25·3	9·1 ± 0·5

are remarkably similar. These results are in accord with a dissociative mechanism accompanied by only slight effects of solvent structure, in line with other evidence on substitutions of these ions in water.[3] The values of $\Delta V^{\ddagger}$ may be compared with values of *ca.* 10 cm^3 mol^{-1} for the unimolecular decompositions of diazonium salts and of t-alkylsulphonium salts, which are likewise dissociations of cations, in water.[4]

A full report will be made elsewhere. We acknowledge the help of Dr. P. A. Tregloan and discussions with Dr. D. N. Hague.

(*Received, September 14th,* 1971; *Com.* 1605.)

E. F. Caldin, J. E. Crooks, and B. H. Robinson, *J. Phys.* (*E*), 1971, **4**, 165.

[2] E. F. Caldin, M. W. Grant, B. Hasinoff, and P. A. Tregloan, to be published.

[3] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2191, 2198.

[4] K. R. Brower, *J. Amer. Chem. Soc.*, 1960, **82**, 4535; K. R. Brower and J. S. Chen., *ibid.*, 1965, **87**, 3396.